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MATERIALS AND METHODS FOR LARGE-AREA SOLAR CELLS

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G. Neal, T. Rabolt (first year only), and R. S. Silver (3 months)

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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACTS NAS 7-202 AND NAS 3-2796

RADIO CORPORATION OF AMERICA
RCA LABORATORIES
PRINCETON, NEW JERSEY

FINAL REPORT

for the period

1 October 1962 to 30 September 1964

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ABSTRACT

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GaAs polycrystalline films have been grown on molybdenum sheet. Attempts to produce p-n junctions in these films have failed because of rapid impurity diffusion at defects. Barriers formed on these films at room temperature by the vacuum evaporation of Cu_2Se have given 3.9% sunlight efficiency. GaAs films formed by flash evaporation and sputtering have shown high resistivity and anomalously high optical absorption. GaAs films on Al foil have given 0.1% efficiency with Cu_2Se barriers and promise a 50 watt/lb power-to-weight ratio. A new photovoltaic effect has been discovered which may be used for direction sensing.

Author

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less than the band-gap; an ill-defined change of adsorption at the band edge; and high resistivities.

All attempts to make p-n junctions in the polycrystalline gallium arsenide layers have failed, the current-voltage characteristics showing excessive leakage. This we attribute to rapid impurity diffusion along some defects in the gallium arsenide films. It was hoped that fast flash evaporation of gallium arsenide would permit the formation of a p-n junction before diffusion could cause short-circuiting. Flash-evaporated films of gallium arsenide have shown anomalous optical properties and high resistivity, being in this respect similar to sputtered films of gallium arsenide.

A study of barrier formation by low-temperature processes was started. The techniques of forming the conducting films of cuprous sulphide and cuprous selenide have been worked out. With cuprous sulphide the optimum compromise between sheet resistance and optical transparency should yield a cell with a sunlight efficiency of between 2% and 3%. By using cuprous selenide, which gives somewhat better results, and by improving the gridding and perhaps using an antireflection coat, it is believed that an efficiency greater than 5% can be achieved in areas of the order of 1 cm^2.

The films on aluminum at present show a high resistance when measured through the films to the substrate. Efficiencies of the order of 0.1 percent have been achieved in very early studies and power-to-weight ratios greater than 50 watts per lb seem possible in the near future.

The current-voltage characteristics for cuprous sulphide layers on both single-crystal and polycrystalline films of gallium arsenide have been studied in detail. They have the same form as similar metal-to-semiconductor barriers. A forward current at small bias is higher for the polycrystalline case which is why the open-circuit voltage drops off faster at reduced illumination than in the single-crystal cells.

During the course of this work a new photovoltaic effect was found in some semiconductor films. In this effect, the photovoltage increases as the angle of illumination departs from the normal to the film. Voltages higher than the band-gap have been observed. While the effect has potential applications in direction sensors, it does not provide a method for efficient power conversion because of the high resistance of the films.

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SUMMARY

The purpose of the program is to investigate materials and methods for the fabrication of large-area solar cells. The goals of this program are to have efficiencies higher than 5 percent, films that can be made up to one square foot in area, flexible cells, and relatively inexpensive production costs.

Gallium arsenide was chosen for greatest effort as the active semiconductor since, theoretically, its band-gap might be expected to provide an optimum compromise between short-circuit current and open-circuit voltage under solar illumination. Its high optical absorption offered the further potential advantage that only a thin film would be needed to obtain complete absorption of the incident sunlight.

Polycrystalline n-type gallium arsenide films, typically 4 mils thick, have been grown on 1-mil molybdenum sheet. These films are frequently cracked and are variable in their electrical properties. Enough acceptable ones have been made to permit the preliminary evaluation of barrier cells (see below). More recently, polycrystalline n-type gallium arsenide films from 5 to 10 microns thick have been made on 1-mil aluminum foil. These films show a photovoltaic response and are, of course, much lighter than the above-mentioned films on molybdenum.

It was hoped that sputtering would permit the deposition of gallium arsenide films at lower substrate temperatures giving a wider choice of substrates and reducing thermal strains and cracking. All sputtered films have shown: an anomalously high optical absorption, particularly at energies

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The barrier-forming techniques mentioned above were applied to cadmium telluride, cadmium sulphide, indium phosphide, silicon, and germanium in some exploratory experiments. The results did not suggest that any of these materials would be better than gallium arsenide in a solar cell.

I. INTRODUCTION

This report covers the work of the last two years including Contract NAS 7-202 (1 October 1962 to 30 September 1963) and Contract NAS 3-2796 (1 October 1963 to 30 September 1964). It gives major emphasis to the work of the last six months since much of the earlier work was exploratory of approaches to the problem which have since been abandoned or which are included in the present work.

There are many reasons for attempting the construction of a thin-film, large-area solar cell for use in satellites. The requirements for power continue to increase and hence the total power supply area must increase. This eventually implies an unfurlable or inflatable array, made preferably with flexible cells. The cells should be thin to minimize their weight. They should be simpler to make and to mount than the present single-crystal silicon and gallium arsenide cells to reduce production and assembly costs.

Eventually, a thin-film, large-area solar cell must be judged on a number of factors. These will include: efficiency, power-to-weight ratio, flexibility, radiation resistance, ruggedness, stability (both on earth and in orbit), and cost to make and assemble. These factors, and trade-offs between them, can only be estimated by making actual solar cells. The general purpose of the present study was to investigate materials and methods for the fabrication of large-area solar cells. A more specific (and probably more realistic) goal of the program is to develop cells with efficiencies above 5%, potential areas of the order one foot square, flexible and with relatively inexpensive production costs.

The technical situation immediately prior to the commencement of the contract will now be described briefly. The II-VI compounds CdS and CdTe had already shown promise. Small-area (~ 1 cm^2) cells of CdS had shown efficiencies in the range 4% to 5% (RCA, Harshaw) and larger-area cells (approximately a few square inches) had shown efficiencies in the range 1% to 2% (Harshaw and RCA). These cells deteriorated on exposure to a humid atmosphere. CdTe cells had shown efficiencies of about 2% (G.E.). At RCA Laboratories, attention had turned to GaAs as a potentially suitable semiconductor for large-area solar cells. Theoretical considerations[1] had shown that the band-gap of GaAs might be near optimum for single-crystal cells. While the theory

could not be extended to polycrystalline cells, since the form of the diode equation could not be predicted for them, yet at least GaAs seemed to offer the most latitude for a deterioration in efficiency if that had to be anticipated. Secondly, the high optical absorption of GaAs indicated that very thin films ($\sim 10^{-4}$ cm) would give complete absorption of sunlight and hence permit weight reduction. It is only very recently (see Section II-B) that we observed encouraging photovoltaic activity in such thin films. Prior to the contract, experimental work had been done on GaAs film formation. Molybdenum and tungsten sheet was used as substrates, and in the method finally adopted the compound is transported across a small gap down a temperature gradient[2]: Ga as Ga_2O which reduces on the substrate and As as the vapor.[3,4]

In the early part of the contract period attention was focused on GaAs film growth. The effects of furnace temperature, source crystal doping, precoating of the substrate, and partial pressure of water vapor in the hydrogen flowing through the furnace were studied.[5] Methods were developed for making both n- and p-type GaAs films.

An important practical point now arises. It is very difficult to make significant physical measurements on these films. In a solar cell the current runs normal to the film, and the state of the top 10^{-4} cm of the film (doping, lifetime, mobility), will be crucial to the cell performance. In the usual Hall and resistivity measurements the current runs along the film encountering the grain boundaries in a different way and being in no way specially affected by the critical top 10^{-4} cm of the film. There is the further problem that the film must either be separated from its metal substrate or grown on an insulating substrate. The latter approach may change the film properties.

The electrical measurement most commonly used is to observe the current-voltage (I-V) characteristic through the film using a rectifying pressure contact such as a gold dot for n-type films. This is repeated with a light shining on the contact perimeter. Such an observation indicates whether the resistance through the film is high or low and if the contact to the substrate is Ohmic.

As discussed elsewhere in this report the optical absorption spectra of films have given revealing information.

The GaAs films on molybdenum were less uniform from point-to-point on a given film, and less reproducible from film-to-film than we could wish. They

were also frequently cracked. Nevertheless, enough "well-behaved" films could be obtained to permit attempts at the construction of small (~ 1 cm^2) solar cells. Emphasis was given to this approach for several reasons: by comparing the performance of thin-film GaAs cells with single-crystal cells information could be obtained about the films which could not be obtained by direct measurements on them; it was considered important to see if thin-film GaAs would yield 5% efficiency before tackling the problems of flexibility, large area, and low production cost.

At first, attempts were made to make a p-n junction cell both by growing a layer of one conductivity type on a film of the other type or by diffusion.[6] While photovoltaic responses were seen, the cells were all leaky and had efficiencies much less than 1%. It was suspected that in the times and at the temperatures needed to make these structures, rapid impurity diffusion at grain boundaries caused short-circuiting. Some evidence[7] to support this view was found in the study of a Zn-diffused, melt-grown, polycrystalline cell.

It seemed possible that these difficulties could be avoided if the p-n junction could be made fast enough at a low enough temperature. For this reason we began the study of the fast flash evaporation of GaAs--work which is reported in Section II-C.

There were some reasons to believe that the cells made with II-VI compounds were barrier cells (i.e., contained a rectifying junction in one semiconductor caused by the juxtaposition of another chemical phase) and not p-n junctions. We therefore began to investigate materials and methods for forming barriers on GaAs (both single crystal and films). Most of the materials were either too resistive (MoO_3, SnS, Cu_3P, Cu_2S) or unstable (CuI), or decomposed before evaporation (NiO, PbO, NiS).[8] Cu_2Se has shown the best compromise between optical transparency and sheet resistance to date. The work on this material is reported in Section III.

Work was also started on the sputtering of GaAs in the hope that more uniform films could be produced at a lower temperature which in turn would permit a wider choice of substrates and a reduction in thermal strains. This work is reported in Section II-C.

Detailed measurements[9] were made of the forward current I as a function of bias voltage V for a number of Cu_2S barriers on both single-crystal GaAs and polycrystalline GaAs films.

Operationally, it was possible to fit the curves (over a limited range) with an equation of the form

$$I = I_0 \; (e^{qV/\alpha kT} - 1)$$

Both I_0 and α are bigger for the polycrystalline films than for the single crystals. Electrical measurements have not distinguished this barrier from that which would be formed by a metal.

At the beginning of the contract period some work was done on the growth of GaP layers,[10] for two reasons. First there was the possibility of making a GaP-GaAs heterojunction. The structure was made but did not behave in accordance with our expectations.[10] GaP films have to be grown at a higher temperature than GaAs which again suggests that grain boundary diffusion will give trouble, and there was also evidence[10] that the electrical junction was not at the chemical interface. The second reason was that a higher band-gap material might give a higher V_{oc} (open-circuit voltage) at an acceptable efficiency and would have smaller resistive losses since it would operate at lower current. A reduction in manpower terminated this part of the program.

During the course of the project it was discovered that some highly resistive GaAs films would develop a photovoltage across the film which had zero value for normal light incidence but which increased to values greater than the band-gap as the illumination was made more oblique.[11] The high resistance of these films makes them very inefficient as energy conversion devices, but they have potential application as direction sensors.

II. GALLIUM ARSENIDE FILMS

A. GALLIUM ARSENIDE ON MOLYBDENUM

In this period we have continued to use the same basic method of film formation[12] but have tended to standardize the following parameters:

(a) Source temperature $\sim 790^{\circ}$C

(b) Substrate temperature $\sim 700^{\circ}$C

(c) Transport gas: hydrogen bubbled through water at 0°C

Under these conditions the growth rate is between 3 and 4 microns per hour.

While the basic mechanism of film growth involves the chemical transport of gallium as Ga_2O and the transport of As as the vapor, for simplicity, we shall refer to this method of film growth as vapor growth.

When bare molybdenum is used as a substrate and a Cu_2Se barrier cell is made on the film, the characteristic (particularly at higher illumination levels) looks like curve (a) of Fig. 1. Since molybdenum, evaporated onto n-type gallium arsenide forms a rectifying contact,[13] it was thought that the film was not making Ohmic contact to the molybdenum substrate. Thus, the cell behaves like two diodes back-to-back. This effect can be overcome (Fig. 1,
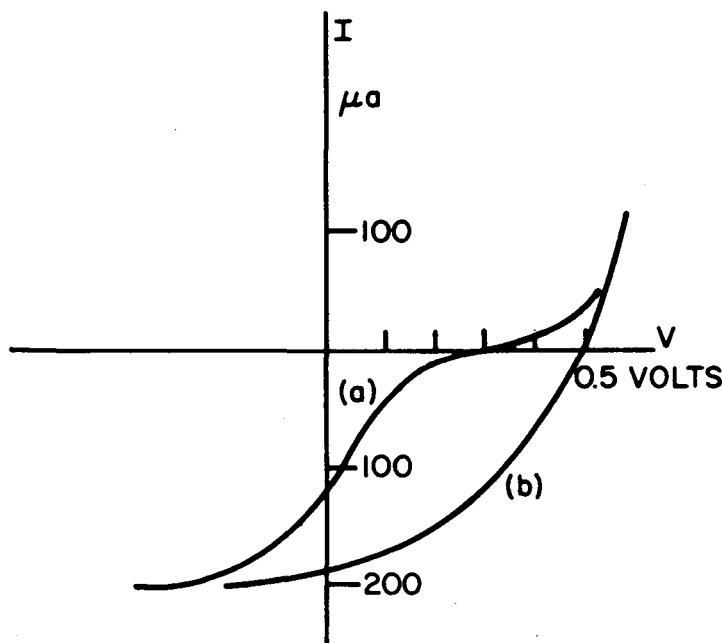

Fig. 1. I-V characteristics under 4-mV illumination. (a) Without tin pre-coat; (b) With tin pre-coat.

curve b) in two ways: by evaporating tin onto the source crystal or by evaporating tin onto the molybdenum foil prior to film growth. The former method has the disadvantage that the amount of tin transported decreases in successive runs so that the "back-to-back" effect eventually reappears, and we have therefore standardized on the latter method.

In one experiment, only one part of the molybdenum foil was pre-coated with tin. Figure 1 shows the diode characteristics from the coated and un-coated areas. This shows that the coated area has a more nearly Ohmic contact between the Mo and film. The GaAs layer over the tin showed laterally larger crystals than elsewhere, suggesting that the tin pre-coat also influences the nucleation of the layer.

Tin layers, which varied from almost opaque to barely discernable when simultaneously deposited on glass, have been used. In this thickness range the I-V characteristics of completed solar cells have been the same. This requires further study, however.

There is no reason to suppose that the tin has reduced the incidence of cracking referred to previously.[14] As will be seen later (Section III-B and Fig. 9), the GaAs film properties will show undesirable variations, but enough "well-behaved" films can be produced so that the study of barrier cells has not been unduly impeded.

B. VAPOR-DEPOSITED GaAs FILMS ON Al SUBSTRATES

In the interest of lightweight flexible substrates we have begun to deposit GaAs films on aluminum. In fact, several films have been deposited on "Reynolds Wrap". The substrate temperatures are between 450° and 660°C. The furnace and technique are similar to those used for Mo substrates, except that a quartz spacer between source and substrate enables the lower substrate temperatures to be achieved. These films are much thinner than those grown on Mo, the thicknesses being between 5 and 10 microns. The films are almost always n-type. To check the current-voltage characteristic and the light response, 0.040-in. Cu_2Se circles are evaporated onto the films. One such characteristic is shown in Fig. 2. The efficiency is estimated to be about 0.1 percent. The series resistance of the cell shown in Fig. 2 is about 1000 ohms. This sets a serious limitation on the efficiency. To determine whether this high series resistance could be caused by back-to-back junctions in the
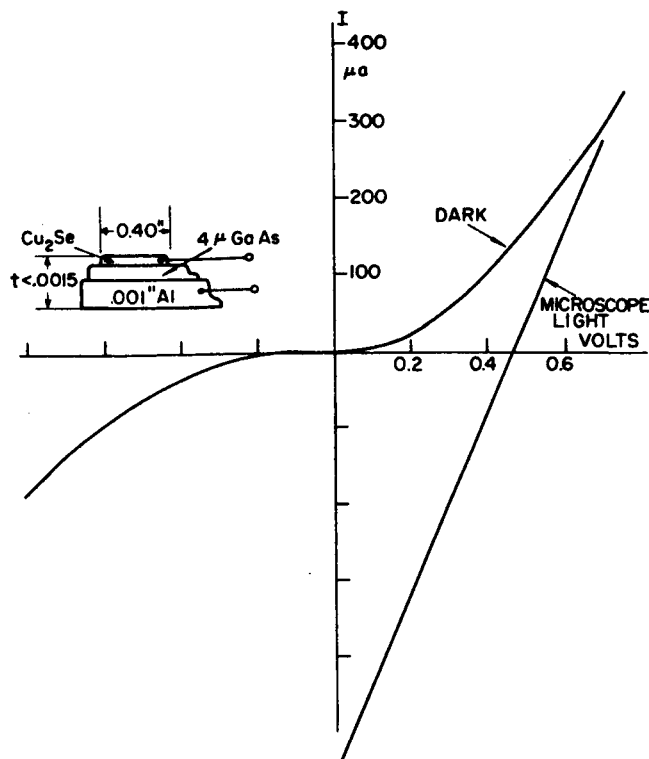
Fig. 2. I-V characteristics of GaAs on Al foil.

film, a spectral response measurement was made of the device in Fig. 2. The result is shown in Fig. 3. Beyond the band edge (0.9 micron) the normal p-on-n barrier response appears. But below the band edge there is an anomalous n/p response. This response must be coming from an n/p junction or barrier below the top barrier. A model which will explain this is shown in Fig. 4. It is speculated that a p-type layer, which for some reason absorbs light below the band edge, exists between the regular n-type film and the substrate. An alternative explanation is that we are observing electron emission from the Al substrate. We are unable to distinguish between these hypotheses.

C. SPUTTERED AND FLASH-EVAPORATED FILMS

As previously stated,[15] it was hoped that GaAs films could be produced at lower temperatures by sputtering, thus reducing thermal strains and cracking and allowing a wider choice of substrate material. It was also hoped that fast flash evaporation would permit p-n junction formation in so short a time and at a low enough temperature that grain boundary diffusion would not cause short-circuiting.

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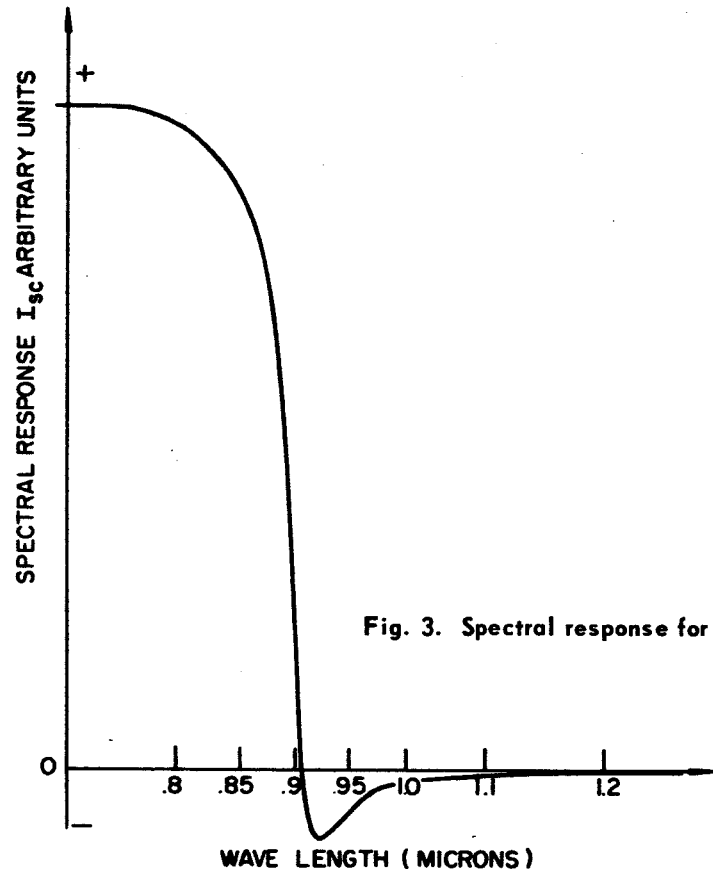
Fig. 3. Spectral response for cell shown in Fig. 2.
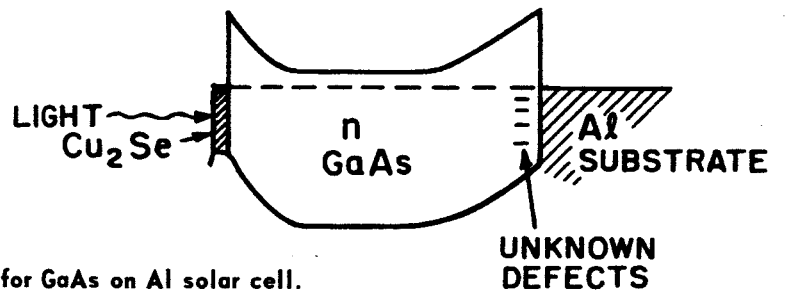
Fig. 4. Proposed band-gap scheme for GaAs on Al solar cell.

Insofar as both of these methods are a new approach to GaAs film formation they are worthy of study in their own right.

1. Sputtering Apparatus

Figure 5 is a schematic diagram of the sputtering apparatus which is operated in the conventional glow discharge sputtering manner. The massive aluminum cathode electrode is covered with a 10-mil-thick high-density alumina coating and can be water-cooled. The source material consists of polycrystalline GaAs wafers glued to a tantalum plate by means of silver-doped epoxy; the

11
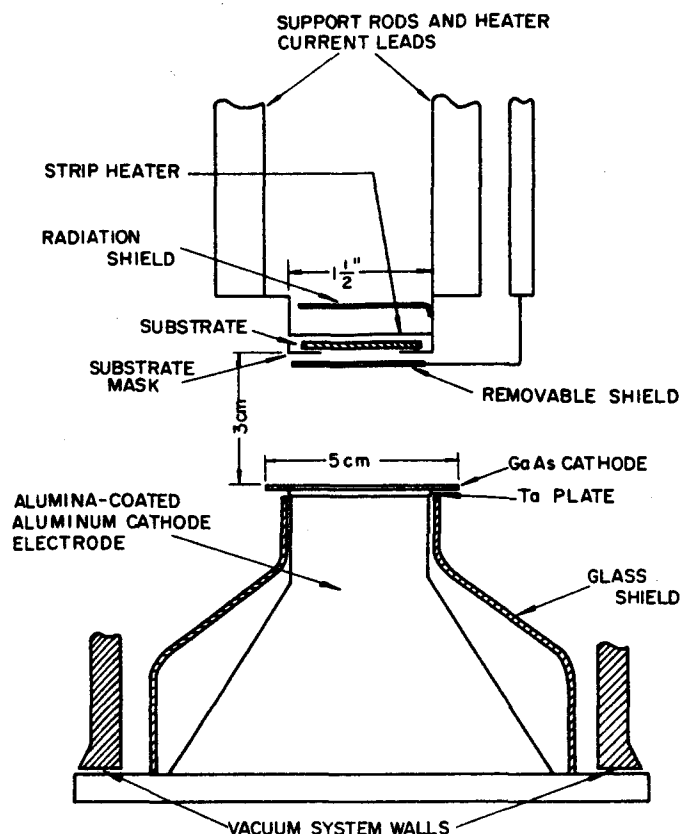
Fig. 5. Schematic of sputtering apparatus.

tantalum plate screws into the aluminum cathode. Three GaAs wafers placed side by side make up a square approximately 5 cm on a side. An earlier method, whereby the GaAs wafers were attached to a nickel plate by means of indium solder, introduced many more impurities (including a high nickel concentration) into the films. The removable substrate shield and the substrate holder and heater are constructed of sheet tantalum and ceramic; the substrate holder exposes a flat anode area in the form of a square approximately 1-1/2 in. on a side.

The following operating conditions are typical:

Current - 10 to 15 mA

Voltage - 1900 to 2300 V

Argon pressure - 55 to 65 microns Hg

Substrate temperature - 250 to 600°C

Cathode-substrate distance ~ 3 cm

Deposition rate - 160 to 240 Å/min.

Argon flow rate - 1 to 3 ml/min.

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The standard tank argon is passed through a desiccant. The only impurity in the argon detected by a residual gas mass spectrometer on the vacuum system was about 0.025% nitrogen.

2. Flash-Evaporation Apparatus and Procedure

A preliminary description has been given.[16] In its present state (Fig. 6), the source heater consists of a 0.001-in. tungsten sheet bent into the form of a boat. The connection and support for the source is a 0.080-in.-diameter
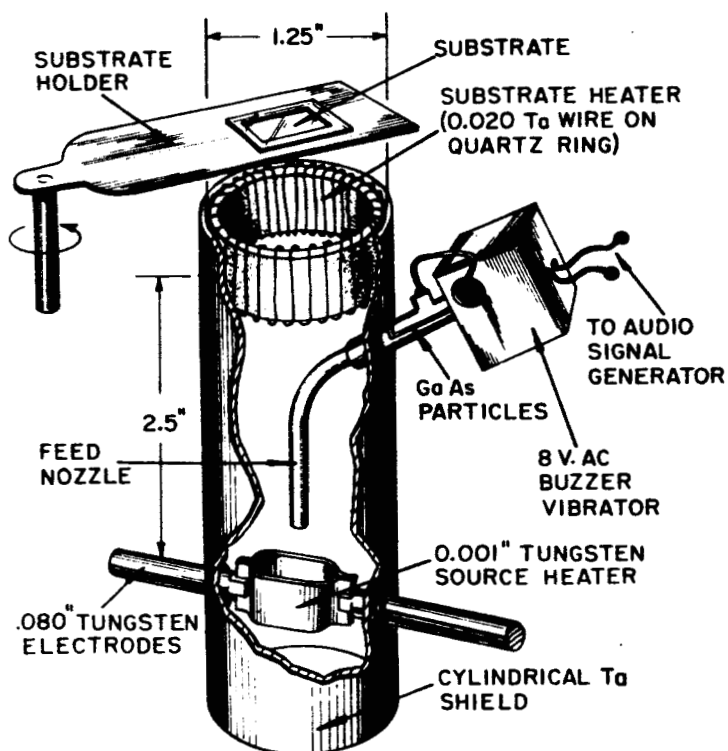
Fig. 6. Flash evaporator.

tungsten rod with notched ends into which the edges of the boat are inserted. A cylindrical tantalum heat reflector surrounds the source heater. Mounted at the top of this reflector is the substrate heater. It consists of a grooved quartz ring on which is wound a 0.020-in.-diameter tantalum heating wire. The "feed" mechanism consists of a V-shaped tantalum chute whose end is shaped into a nozzle. The particles are vibrated through the chute and then drop into the source heater. A fine mesh made of 0.001-in.-diameter wire at the top of the source heater screens many of the particles which are splattered out of the boat. The chute is mechanically attached to the vibrating arm of

an ordinary 8-volt household buzzer to provide the vibrations. In practice, it would be convenient to control the frequency and amplitude with an audio oscillator which in turn provides for control of the feed rate. The substrate is mounted on a movable arm above the substrate heater. It can be moved in and out of the path of evaporation and the source-substrate spacing can be varied. The entire assembly is installed in a bell jar evaporator where pressures on the order of 10^{-5} mm Hg are achieved.

The bulk GaAs is ground into powder with a mortar and pestle and sifted through a series of sieves to select the appropriate particle size. If the particles are too large, true flash evaporation cannot be achieved with the usual source temperatures. If the particles are too small they tend to splatter out of the heater. Particle diameters from 0.010 to 0.014 in. have been found to work best. No special cleaning procedures, like etching, have been used on the particles because it was felt to be impractical because of the large surface areas involved. The materials with which the particles are handled (mortar and pestle, sieves, etc.) are kept clean, however. It has been found experimentally that the most uniform doping of the films is achieved by using doped source material. This procedure enables the most uniform proportion of dopant and matrix to be maintained throughout the deposition. Therefore, specially prepared ingots of GaAs doped to 1 to 3 percent with the appropriate dopant are used to prepare the source powder. The usual dopants for GaAs were tried before it was found that manganese works best for p-type dopant and tin for n-type dopant.

The source powder is placed in the chute, the substrate in the substrate holder, and the bell jar is closed and evacuated. The usual procedure is to outgas the source heater and then the substrate by means of the substrate heater. For the actual film deposition, the source heater is brought to about 1600°C. The substrate is then brought to deposition temperature (200 to 600°C depending on the object of the experiment) and the particle feed vibrator is started. The thickness is estimated through experience in observing the transmission of the film on glass.

It was soon found that although the film could be deposited at a high rate (~ 2 to 3 microns per minute), the quality of the film is dependent on the rate of deposition. X-ray diffraction has uncovered inhomogenities in films grown at these rates. These films also show abnormally high optical

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absorption. Therefore, the idea of depositing a good-quality film in a short time to prevent grain boundary diffusion is difficult to achieve in practice at present. The deposition rate at which most of the films are made is around 1,000 Å/minute. This is an average rate since it has never been possible to achieve a truly uniform rate of particle feed.

After deposition, the substrate is cooled by turning the heaters off at the desired rate. The cool-down time averages about 1/2 hour. Substrates on which films have been grown include glass, molybdenum, single-crystal GaAs, GaAs vapor-grown films, and calcium fluoride.

3. Results

a. <u>Structural Properties</u> - All films analyzed by x-rays show only single-phase GaAs (the possible existence of a small amount of a metastable hexagonal phase of GaAs is discussed later) except for a few flash-evaporated films which were very highly doped with Mn. For these, x-rays detected a small concentration of a Mn_2As phase. Crystallite size as measured by x-ray line broadening is a strong function of substrate temperature. The results of quantitative measurements on three sputtered films are shown in Table I. The absolute values reported here may be in considerable error due to approximations

TABLE I

Average Crystallite Size

Substrate Temp. (^oC)	Film Thickness (microns)	Average Crystallite Size (Angstroms)
400	7.14	350
500	3.18	600
590	6.20	>2000

to take into account the shape of the diffraction peaks, but relative values should be quite reliable. The values reported here are comparable to values reported by Harvey and Heyerdahl[17] (240 Å at 400°C, determined by electron microscopy) and Davey and Pankey[18] (< 240 Å at 300°C, determined by x-ray line broadening).* No dependence of crystallite size on film thickness for thick-

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* "Crystallite Size" as determined by x-ray line broadening is really a measure of the number of atomic planes over which the repetition is nearly exact; thus, this size may be smaller[18] than crystal size as normally understood in terms of a macroscopic picture.

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nesses between 0.2 and 8 microns has been noted. Films deposited at room temperature are completely amorphous. A sputtered film deposited at 320°C showed a weak crystalline phase, but because this film was quite thick (4.1 microns) it was concluded that most of this film was amorphous.

A slight amount of preferential orientation (most commonly [111]) is usually observed for sputtered films on glass. In general, the amount of preferred orientation increases with substrate temperature. Flash-evaporated films are more commonly random - oriented, except for some films produced near 600°C which show some [111] preferred orientation. Only two films have been deposited onto single-crystal GaAs [111] substrates to date, one by sputtering and one by flash evaporation. X-ray analysis indicates that these films grow epitaxially, but no attempt has yet been made to grow such films below 450°C. Richards, Hart, and Gallone,[19] and Müller[20] have studied the epitaxial formation of GaAs on Ge by flash evaporation and found that twinned epitaxy occurred above 400°C and untwinned epitaxy occurred above 500°C. However, Francombe and Schlacter[21] report that epitaxy may be obtained at lower temperatures by sputtering.

In many of the films, particularly those produced at the lower substrate temperatures, a weak x-ray diffraction peak appears at a position where no reflection from cubic GaAs should occur, but where one would expect to see a $(10\bar{1}0)$ reflection if a hexagonal phase of GaAs existed. The existence of a metastable hexagonal phase in flash-evaporated GaAs films has previously been seen by Müller[20] in electron diffraction studies. He also observed this phase predominantly in the lower temperature films where the atomic surface mobility is low and defects are frozen in as they form. The hexagonal phase is associated with a high density of stacking faults and is interpreted as a periodic arrangement of stacking faults. A very weak $(10\bar{1}0)$ x-ray diffraction peak has been seen in some films sputtered at temperatures as high as 550°C.

b. Optical Properties - Measurements of optical density vs. wavelength below 2.5 microns were obtained from almost all films deposited on transparent substrates using a Cary Model 14 Spectrophotometer. The interference maxima and minima in these curves provide the primary means for determining film thickness. The index of refraction is taken from Marple's data on bulk single crystals[22]; this will introduce a small error in the calculated thickness if the true index of refraction of the films differs from Marple's values. However,

Tolansky measurements on a few of the sputtered films indicated that this
difference must be small for crystalline films; amorphous films deposited at
room temperature appeared to have a higher index of refraction by as much as
20 to 30%.

The absorption coefficient vs. wavelength was computed from the optical
density measurements for many of the films. The procedure for this calcula-
tion is essentially that described by McLean,[23] except that the variation of
reflectivity with wavelength reported by Ehrenreich, Philipp, and Phillips[24]
is taken into account. When it appears from the shape of the optical density
curve that the films are not absorbing between 2.0 and 2.5 microns (most
films), the absolute value of reflectivity is calculated from the optical
density. Otherwise, the absolute values reported by Ehrenreich et al. are
used. The high absorption coefficients found near the band edge are quite
insensitive to errors in the reflectivity. The major source of error in this
region is probably the uncertainty in film thickness. Scattered light from a
"rough" surface can also introduce a significant error; therefore, the surfaces
of films which appear to scatter light are polished before obtaining the
optical data.

Figure 7 shows the dependence of the absorption coefficient on wavelength
for a number of GaAs films formed under various conditions (amorphous sputtered,
crystalline sputtered and flash-evaporated, thin vapor-grown, thick vapor-grown,
published single crystal[25]). In all cases, the sputtered and flash-evaporated
films do not exhibit a well-defined absorption edge. In general, the absorp-
tion coefficients for these films are higher than the single-crystal values
at all wavelengths; the decrease of the absorption coefficient for wavelengths
above the normal band edge is very gradual compared with the decrease at the
single-crystal absorption edge. Harvey and Heyerdahl[17] report finding this
same general shape in optical density measurements on GaAs films vacuum-deposited
from separate Ga and As sources. Howson[26] also finds this same result for
evaporated films produced by a modification of Günther's three-temperature
method.[27] The absorption coefficients for the two epitaxial films produced to
date (one sputtered, one flash-evaporated) appear to be similar in all respects
to the polycrystalline films. In addition, slight interference maxima and
minima were detected in the optical density curves of the epitaxial films.
These gave the correct thickness of the deposited layer, and therefore indicate

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Figure 7

10^5

ABSORPTION COEFFICIENT $(cm)^{-1}$

10^4

G-2

F-47

#69

LEGEND:

MO. 2: 4 MIL VAPOR GROWN

#69: 2.7 MICRON " "

#38: 5.0 " " "

G-25: 6.2 " SPUTTERED

G-2: AMORPHOUS SPUT-
TERED

F-47: CRYSTALLINE FLASH
EVAP.

F-47 IS TYPICAL OF MANY
CRYSTALLINE SPUTTERED
AND FLASH-EVAPORATED
FILMS

10^3

#38

G-25

SINGLE CRYSTAL
(AFTER STURGE)[25]

MO. 2

10^2

.5   .6   .7   .8   .9   1.0   1.1   1.2
WAVELENGTH (MICRONS)
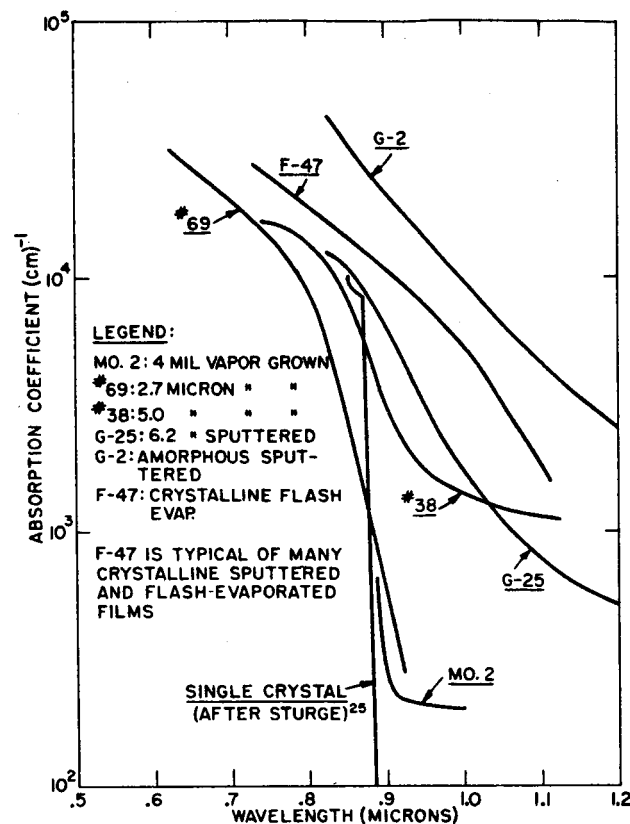
**Fig. 7. Variation of absorption coefficient with wavelength
for various films.**

that an optical discontinuity exists at the interface between the single-
crystal GaAs and the epitaxial film; either the film has a significantly
different index of refraction from that of the single-crystal substrate, or
there is a very thin interfacial layer (such as an oxide), having significantly
different optical properties from GaAs, separating the film and the substrate.

The absorption coefficients for the vapor-grown films more nearly approxi-
mate the single-crystal values; the decrease above the normal band edge is
steeper than either the flash-evaporated or sputtered films, and the absorption
coefficients for wavelengths below the normal band edge are lower than the
single-crystal values, at least for the thin vapor-grown films. Sputtered
film G-25 and vapor-grown film No. 38 (Fig. 7) were prepared as closely as
possible under identical conditions of substrate temperature and thickness
(550 to 600°C, 5 to 6 microns), and yet the differences in optical absorption
properties as described above are readily apparent.

No clear correlation between absorption coefficient and substrate tempera-
ture has been established for either flash-evaporated or sputtered films.

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However, the results suggest that such a correlation may exist, although many exceptions can be found. Figure 8 shows the absorption coefficient vs. wavelength for three films sputtered at 400, 500, and 590°C, and indicates that the higher temperature films have lower absorption constants. Howson[26] also noted a similar correlation is his GaAs films. Figure 8 also illustrates the absorption coefficients of these same films after annealing at about 600°C for 24 hours under an arsenic pressure of about 10 torr. The absorption coefficients decreased, becoming almost identical at wavelengths below the normal band edge, and approximating very closely the single-crystal values at wavelengths just below the normal band edge. However, x-ray analyses of these
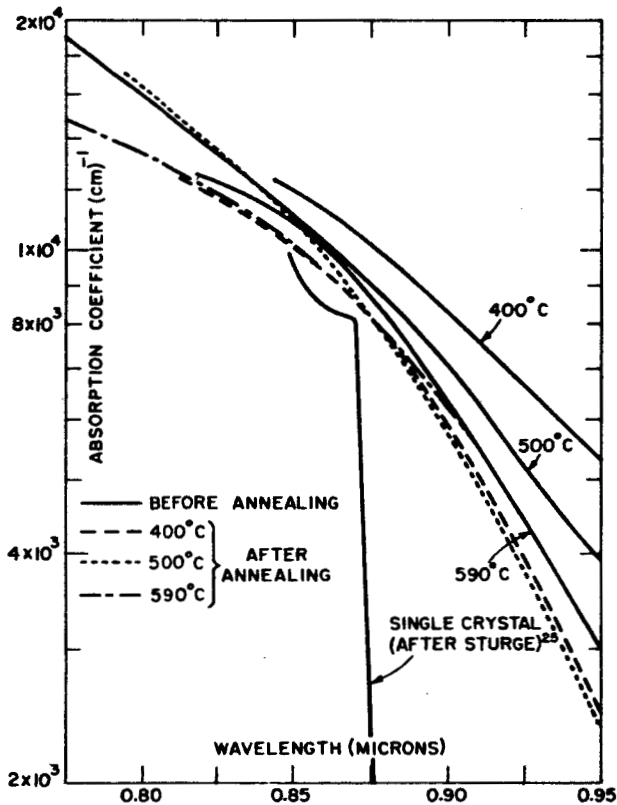
Fig. 8. **Effect of substrate temperature and annealing on the optical absorption coefficient.**

films after annealing indicate that no change in line broadening or film structure has occurred. Harvey and Heyerdahl[17] also found no change in crystallite size upon annealing. However, an exception to this result occurred for one flash-evaporated film which initially consisted of very small un-oriented crystallites (believed to be nearly amorphous). After annealing at 630°C for 21 hours under an arsenic pressure of about 10^{-2} torr it converted

from p-type to n-type conductivity and the crystallite size increased (to a few hundred Å) and showed a slight (111) preferred orientation. The optical absorption coefficient also decreased, but remained substantially above the single-crystal values.

c. Electrical Properties - Measurements of conductivity type (n or p) are made by means of a thermal probe. Electrical resistance measurements are made between 40-mil diameter pressed gold dots placed 2 to 5 mm apart on the film surface. By checking such measurements against accurate measurements by means of a four-point resistivity probe, it was found that the gold-dot measurements give the correct sheet resistivity (ohms per square) within a factor of two when the width of the film between contacts is at least as large as the separation of the contacts. Apparently contact resistance is negligible compared with the high resistance found in the films. The absolute values of resistivity reported here are reliable therefore only to within a factor of two. However, the measurement of the variation of resistivity with temperature reported for one sputtered film was a true four-point measurement. The concentration of certain impurities in the deposited films and the GaAs source material was obtained by emission spectrographic analysis.

Both sputtered and flash-evaporated GaAs films which are not intentionally doped are p-type. This result has also been reported for GaAs films formed by other methods.[17,18] However, in contrast to the vapor-grown films and the films studied by Harvey and Heyerdahl,[17] it is difficult to change the resistivity and conductivity type of either the sputtered or flash-evaporated films by adding dopants. Films deposited with normal concentrations (up to the 10^{18} cm^{-3} range) of either n- or p-type dopants have high resistivities in the range of 10^3 to 10^5 ohm-cm. By incorporating very high concentrations of Mn into the flash-evaporated films ($> 0.1\%$), resistivities in the range 10 to 10^3 ohm-cm are obtained. The only n-type films produced (both sputtered and flash-evaporated) contained between 0.1 and 1% tin. These films have always exhibited very high resistivities (10^4 to 10^6 ohm-cm).

There appears to be a correlation between film resistivity and substrate temperature for both sputtered and flash-evaporated films. Although many exceptions can be found, the higher resistivities generally correspond to the higher substrate temperatures; a similar dependence on substrate temperature was found by Davey and Pankey[18] for a lower range of temperatures. Annealing

of three sputtered films in arsenic vapor (see page 19) caused a substantial increase in resistivity without changing the conductivity type (p-type). It can be seen in Table II that the factor by which the resistivity increased varied inversely with the deposition temperature. Similar large increases in resistivity were observed by Davey and Pankey[18] upon annealing their films at 380°C in vacuum. It would appear from changes in both resistivity and optical absorption that the effect of annealing is to make the films appear to have been grown at a higher substrate temperature initially. Only the film structure retains the memory of its true initial deposition temperature.

TABLE II

Effect of Annealing on Resistivity

Substrate Temp. (°C)	Initial Resistivity (ohm-cm)	Final Resistivity (ohm-cm)	Ratio Final/Initial
400	10,000	360,000	36
500	4,000*	80,000	20
590	70,000	470,000	~7
* This film is one of the exceptions to the general rule describing the variation of resistivity with substrate temperature.			

Only one reliable measurement of the variation of resistivity with temperature of a sputtered film has been obtained to date. This measurement confirms the 0.18-eV acceptor level reported by Davey and Pankey[18] at room temperature. Above 120 to 130°C, the Fermi level begins to penetrate more deeply into the forbidden band, but the intrinsic value of 0.7 eV is not seen since the measurements do not extend above 300°C. No sign of the 0.025-eV level reported by Harvey and Heyerdahl[17] at low temperatures is seen.

Only a very few films have been deposited to date (both sputtered and flash-evaporated) on n-type single crystals and vapor-grown films. A very weak light response having p-on-n characteristics was observed in each case. The sputtered films have been too thick (2-1/4 microns) for much light to reach the junction, but as expected, the high resistance of the sputtered layer is a serious problem. In addition, the diode characteristic of the junction was leaky.

A few of the earlier sputtered films which utilized the earlier cathode mounting (GaAs soldered to Ni with In) exhibited the "classical" high-voltage photovoltaic effect, i.e., the polarity of the photovoltage is built into the film and the magnitude of the voltage depends only on the intensity of the light. Using a focused microscope light, up to 22 volts output at room temperature was obtained between contacts one cm apart. This was almost doubled by illuminating through the substrate. The response was not always uniform over the entire area of the film. Rough spectral response measurements indicated that the response began at the GaAs band edge and was essentially constant (per photon) at higher energies (at least to above 2 eV). These films were characterized by an extremely high sheet resistance (10^9 - 10^{10} ohms per square) and very high concentrations of Cu, Ni Fe, Mg, and In impurities (to 0.1% or more of each). No mechanism for the formation of the preferred voltage direction in the films has been deduced. The usual mechanism of oblique desposition would not seem to apply here.

d. <u>Discussion and Conclusions</u> - In almost every respect, GaAs films produced by sputtering and flash-evaporation are indistinguishable from one another. The only difference noted is the greater tendency of the sputtered films to exhibit a slightly preferred orientation. However, considerable differences have been noted between the properties of these films and those of vapor-grown films. Vapor-grown films of either n- or p-type conductivity can be prepared with normal doping concentrations (up to 10^{18} cm^{-3}) and low resistivities (< 100 ohm-cm). Also, these films have optical absorption properties more nearly like single crystals. The differences do not appear to be caused by impurities. The electrical properties of sputtered and flash-evaporated films are relatively insensitive to large variations in impurity content. Also, sputtered films have been prepared containing relatively low levels of impurities (as detected by emission spectrography) similar to those found in many vapor-grown films. (It must be admitted, however, that the electrical properties of the vapor-grown films do not correlate well with impurity content as detected in this way.)

Other possible causes of the different properties of sputtered and flash-evaporated films are various structural defects which may be frozen into the films during the deposition process (both of these processes are more irreversible than the transport growth process). For example, the dependence of

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the intrinsic p-type nature of Ge films on the defects which form in these films during deposition has long been fairly well established. Specific defects which might be suspected in the present case are stacking faults, vacancies, and crystal boundaries.[*] The presence of a high concentration of stacking faults in these films is strongly suspected because of the x-ray evidence for a metastable hexagonal phase and Müller's[20] finding that this phase is associated with a high density of stacking faults. However, the electrical activity of stacking faults in GaAs is not yet known from independent studies. A high concentration of vacancies in these films is also strongly suspected. Davey and Pankey[18] argue that vacancies are responsible for the 0.18-eV acceptor level found in their GaAs films deposited at low temperature ($< 400^{\circ}$C) by the three-temperature method of Günther.[27] They cite the changes in density and reduction in concentration of acceptor centers upon annealing at 380°C. They also cite the results of Aukerman and Graft[28] on the effect of radiation damage on optical absorption in bulk GaAs and Bube's[29] observations of the acceptor levels in bulk GaAs. Although the present results do not agree quantitatively with those of Davey and Pankey[18] (except for the observation of the 0.18-eV acceptor level), there are many qualitative similarities, such as the change in resistivity and optical absorption with substrate temperature and the change in resistivity and optical absorption upon annealing.

In general, both the optical absorption coefficient and resistivity of sputtered and flash-evaporated films varied together upon annealing or changing substrate temperature; that is, any changes in processing which increased resistivity also decreased optical absorption. However, crystallite size, as determined by x-ray line broadening, did not change upon annealing (except for the one nearly amorphous film), although this particle size is a strong function of substrate temperature. In addition, x-ray analysis showed that the two films deposited on single-crystal GaAs substrates (one sputtered, one flash-evaporated) were epitaxial, but the optical absorption coefficients of these films were indistinguishable from those of the polycrystalline films deposited on glass. Although not conclusive proof, these facts suggest that

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[*] Another possibility is discussed in the Appendix.

grain boundaries are not the primary cause of the observed optical and electrical properties of the sputtered and flash-evaporated films: (1) Optical absorption and electrical resistivity of these films do not correlate (upon annealing) with crystallite size as determined by x-ray line broadening. (2) The epitaxial films, which may contain high concentrations of dislocations randomly distributed or aligned (small-angle grain boundaries) and many other defects, but which by their nature cannot contain the normal grain boundaries present in polycrystalline films, exhibit optical properties similar to the polycrystalline films on glass.

Based on the data available to date it is suspected that primarily vacancies, and perhaps also stacking faults, are responsible for the observed electrical and optical properties of the sputtered and flash-evaporated films. These defects would be likely to form equally well in epitaxial and non-epitaxial films. Because the intrinsic electrical properties of both sputtered and flash-evaporated films (high-resistivity, p-type conductivity) cannot be effectively modified by normal dopant concentrations or by other treatments attempted to date, these films are not suitable for thin-film solar cell fabrication; the vapor-grown films currently produced are far superior for this purpose.

III. BARRIER CELLS

A. Cu_2Se FILMS

The technique for forming the Cu_2Se layer differs from that used in forming Cu_2S[30] in that there is no chemical treatment of the film after deposition.

The Cu_2Se is pre-fired in a continuously evacuated quartz tube, both to compact it and to drive off loosely bound selenium. A piece of the charge is then put into an alumina-clad tungsten spiral and pre-fired in vacuum at a slightly higher setting on the Variac controlling the heater current than V_1 (V is Variac setting) mentioned below. The method of determining V_1 and V_2 will be given later. The following schedule for the evaporation was determined empirically to give the lowest sheet resistance for a given optical transmission:

(1) With a shutter over the tungsten spiral, the Variac is turned rapidly to V_1 and held there for one minute. In this time the charge melts and the pressure will rise (typically from 2×10^{-6} torr to 5×10^{-6} torr) and then drop.

(2) The Variac setting is then decreased to V_2 and held there for one minute. There is usually a slight decrease of pressure in this time.

(3) The shutter is opened and the deposition proceeds. We commonly monitor the deposition by measuring the transmissivity of the film to 1.5-eV radiation.

The setting V_2 is chosen to give a 60-percent transmitting film on a slide 12 cm from the tungsten spiral in approximately one minute; $V_1 = 1.25\ V_2$. For a standard tungsten spiral, V_1 is such that the heater current is of the order of 20 amperes.

Films produced in this way have a specific resistivity of 1.62×10^{-4} ohm-cm. A film that is 70 percent transmitting to 1.5-eV radiation has a sheet resistance of 93 ohms per square and is thus 175 Å thick. It is too thin to act as an antireflection coating.

B. CELLS WITH Cu_2Se

The preparation of the cells has now been simplified (compare ref. 31). The etching procedure is:

(1) Etch with 1% bromine in alcohol for 10 seconds.

(2) Wash with alcohol.

(3) Blow dry and immediately mount the film in the vacuum system.

The Cu_2Se layer is then evaporated through a 0.76 x 0.95 cm mask using the technique described in Section III-A. Cu_2Se is simultaneously evaporated onto a glass slide at the same level as the film. This will later allow a measurement of the percent transmission of the Cu_2Se film to 1.5-eV radiation. Subsequently, a gold strip 7 x 0.7 mm is evaporated centrally on the Cu_2Se film to provide an Ohmic contact.

The V-I characteristic of the cell is first examined on an oscilloscope using the small-area 4-mW light. Since the illuminated area is small compared with the area of the Cu_2Se film, it is possible to study the uniformity of the response over different parts of the film. If cracking causes some parts of the film not be connected to the gold, only the active area is used in computing the sunlight efficiency. The area of the gold strip is <u>not</u> subtracted from the active area.

Using the 4-mW light the light-generated current, I_L, is measured at a sufficiently negative voltage so that sheet resistance in the cell does not influence the result. Figure 9 shows a plot of I_L versus percent transmission of the Cu_2Se film. Some of the points fall on or close to a straight line. The corresponding films have been made in both a quartz radiation furnace and in a directly heated furnace, No. 1.[12] A second directly heated furnace, No. 2, has consistently given points below the line. It is possible that this furnace is contaminated since it was used under a wider variety of experimental conditions. The remaining points below the line represent films showing excessive "leakage".

A necessary but not sufficient condition that a Cu_2Se-GaAs cell be efficient is that its I_L vs. percent transmission point lie on the line of Fig. 9. It may lie on this line and still have low efficiency if the forward characteristic shows excessive current, and if in consequence V_{oc} is low.

Figure 10 shows a plot of sunlight efficiency, η, versus percent transmission of the Cu_2Se film for the better cells, i.e., those which have the maximum efficiency for a given percent transmission. These preliminary results suggest that the optimum Cu_2Se film has a transmission close to 60 percent. If the gridding is optimized and an antireflection coat is added, it is
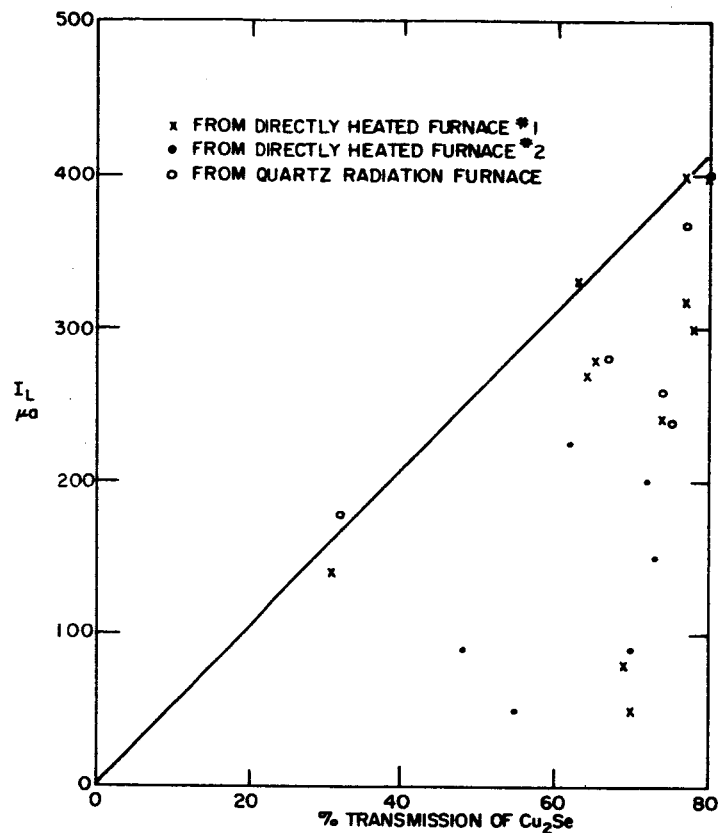
Fig. 9. Light-generated current I_L as a function of percent transmission of Cu_2Se film.

Fig. 10. Efficiency η versus percent transmission of Cu_2Se film.

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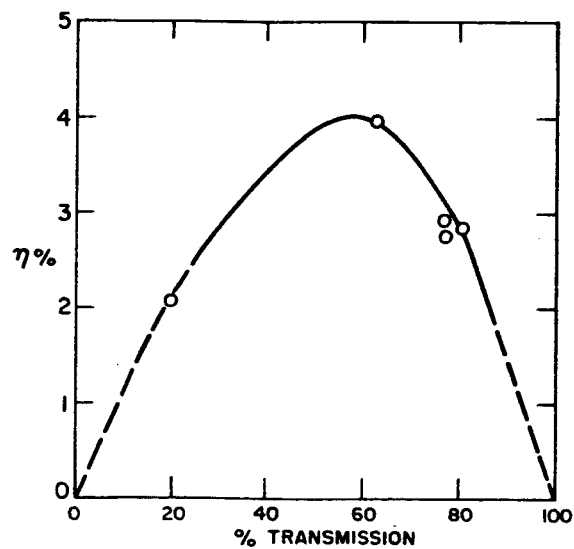
believed that an efficiency of 5% can be achieved with a Cu_2Se barrier on the best GaAs films as currently made. Figure 11 shows the spectral response for one of these cells.

These cells have been stored in plastic boxes for weeks without a change of characteristic. They have also withstood heating to over $100^\circ C$ in a hot air blast without changing characteristics.
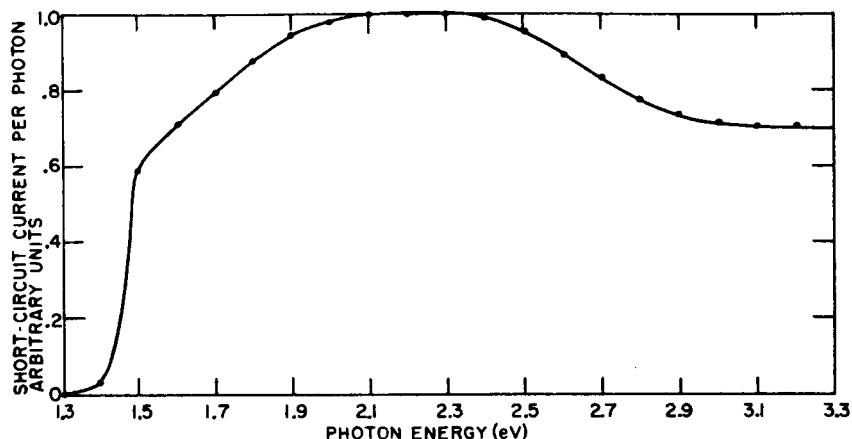
Fig. 11. Spectral response for Cu_2Se barrier cell on GaAs.

C. CELLS WITH Cu_2S

The earlier experience is given in reference 31.

The recognition of the "back-to-back" diode effect and its removal by a tin undercoating (see Section II of this report) suggested that the use of Cu_2S be reviewed.

Some preliminary results indicate that high sheet resistance will limit the efficiency of these cells. The best efficiency to date is still 1.6 percent, but this work continues.

IV. PHOTOANGULAR EFFECT

Since the publication of the complete detailed report[11] on the photo-angular effect, no further work in this area has been done other than to grow an occasional unit and verify its reproducibility.

V. OTHER STUDIES

Continuing the studies of the electrical properties of barriers, measurements were made of junction capacitance as a function of bias for a Cu_2S layer on a polycrystalline GaAs film. The usual plot of $1/C^2$ vs. V, illustrated in Fig. 12, is very different from that obtained with a single-crystal substrate.[32] The intercept with the voltage axis, 1.9 volts, is higher than with a single crystal, and the slope becomes positive at negative biases. Neither of these results is understood. If one applies the usual semiconductor theory to the slope at a small bias a donor density of 3.1×10^{17} cm^{-3} is obtained.

In a separate experiment an attempt was made to lower further the specific resistance of a Cu_2S film on glass by treating it with the vapor over ammonium sulphide at higher temperatures and pressures than are normally used.[30] The film was placed over a beaker of ammonium sulphide in a steel bomb and was heated to $150^\circ C$ at which time the pressure had reached 150 psi. The resistance of the film while in the bomb rose and fell in an irregular fashion. After cooling and removal from the bomb the film resistance had been permanently increased. It was then determined that while ammonium sulphide vapors reduce the resistivity of a freshly evaporated film during the first minute or two of exposure,[30] longer exposure raises the resistivity.
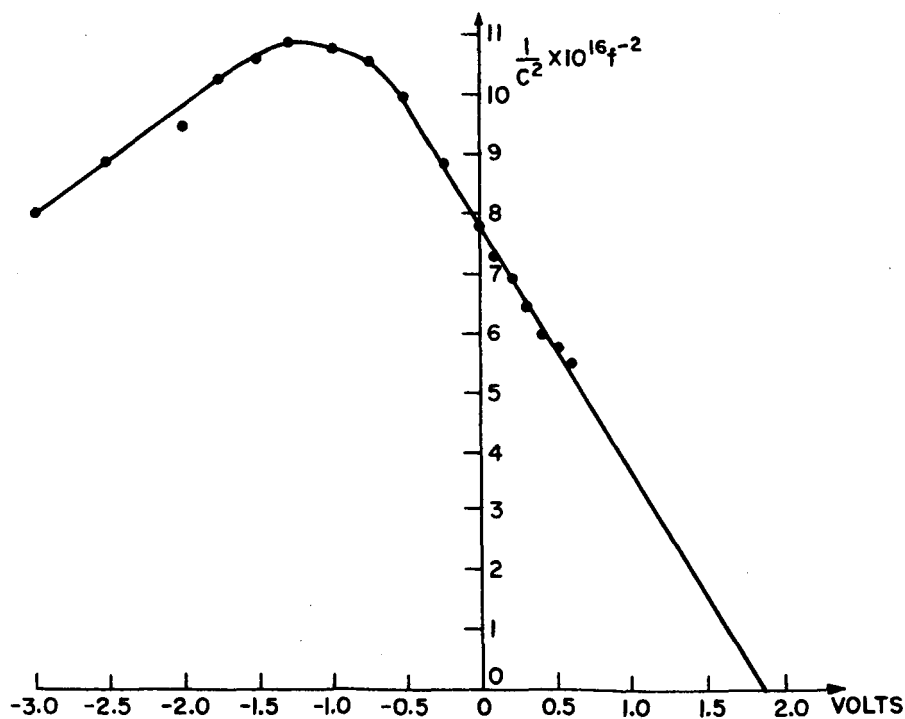
Fig. 12. $\frac{1}{C^2}$: V for Cu_2S on polycrystalline GaAs film.

VI. CONCLUSIONS

It is advantageous to use a Sn pre-coat on the molybdenum substrate when growing n-type GaAs films. Such films, when covered with a Cu_2Se film of appropriate thickness and an antireflection coat, are expected to yield cells with sunlight efficiencies as high as 5%. It is tentatively concluded that Cu_2S layers of optimum thickness will yield cells of lower efficiency than those employing Cu_2Se.

To date, GaAs films formed by sputtering and flash evaporation are not as good for solar cell applications as those grown by chemical transport. They have high resistivity and anomalous (high absorption) optical properties due to an unknown defect. The defect concentration can be reduced (but not sufficiently) by annealing.

Aluminum foil has possible application for light flexible GaAs poly-crystalline solar cells. Power-to-weight ratios of over 50 W/lb seem possible in the near future using these techniques.

VII. RECOMMENDED AREAS FOR FUTURE WORK

1. Study the defect structure of the GaAs films to determine the cause of the anomalous optical absorption and high resistivity.
2. Study fabrication and post-fabrication techniques in order to improve GaAs film characteristics.
3. Continue study of the flexible GaAs cell on aluminum foil.
4. Optimize barrier-type cell using GaAs with a layer of either Cu_2S, Cu_2Se, or Cu_2Te.

ACKNOWLEDGMENTS

APPENDIX

In the body of this report, and in the literature cited there the defect structure of sputtered and flash-evaporated GaAs films has been discussed in terms of the now "classic" list of defects introduced by Seitz[33]: stacking faults, dislocations, and point defects. In this Appendix, we point out that another type of defect may be present in such films: a residue of amorphous material. If this is the case, it becomes understandable why the defects can be reduced in concentration but not removed by annealing at temperatures much below the melting point.

In a vacuum deposition process the semiconductors GaAs, Ge, and Si behave in a very different way from metals or polar compounds of similar melting point. If the substrate temperature is only a little less than one third the absolute melting temperature, the semiconductors condense as amorphous films. The explanation for this and for the structure of the films is to be found in the strength and directed nature of the homopolar bond.

In amorphous germanium, the electron diffraction pattern is consistent with a cross-linked polymeric structure in which the nearest and next-nearest atom distances, and the angle between bonds are close to the values observed in the crystalline state. Due to distortions both in length and angle the bond energies will have a range of values up to those found in the single-crystal state. Therefore, on annealing at higher and higher temperatures one would expect a progressive change rather than a sudden change to the crystalline form. This phase change is much more like that which occurs in the devitrification of glass than it is to an order-disorder transition in an alloy. The key factor is that it requires the _breaking_ of valence bonds. While many of the bonds in the amorphous state are strained, when an atom moves from the amorphous to the crystalline phase, in general, more than one bond will have to be broken. This (even neglecting the added obstacles due to steric hindrance) is an energetically improbable step, since it requires a high activation energy.

It is usually said that Ge films grown on substrates at $350^{o}C$ or higher temperature are crystalline, implying that they are completely in that state. The electron diffraction evidence will neither support nor retract this view, since an amount of amorphous phase of less than 10 percent will not affect the diffraction pattern.

The case of a film grown at a higher substrate temperature, say 600°C, is different from one grown in the amorphous state and then annealed at 600°C. The surface atoms which have just condensed will be less impeded by steric effects from moving into correct positions, but if a small region has condensed in the amorphous configuration it still requires a process of bond-breaking to allow it to enter the crystalline phase. This can be expected to be energetically improbable until temperatures very near the melting temperature are reached. Incidentally, the anomalous Trouton's constant for germanium indicates that bond-breaking is not complete even in the liquid.

These considerations reinforce the view (which can be reached by other considerations) that for the growth of more perfect films a more nearly reversible process must be used, such as growth from the melt, or by chemical transport. For it is only in such a process that atoms incorrectly attached to the solid can escape from it and be replaced by atoms in correct sites.

REFERENCES

1. J. J. Loferski, J. Appl. Phys. <u>27</u>, 777 (1956).

2. Fourth Quarterly Report, Contract NAS 7-202, October 30, 1963, page 11.

3. C. D. Thurmond and C. J. Frosch, paper given at the Meeting of the Electrochemical Society, September 1962, Boston, Mass.

4. M. Michelitsch, W. Kappallo, and G. Hellbardt, J. Electrochem. Soc. <u>111</u>, 1248 (1964).

5. First Quarterly Report, Contract NAS 7-202, December 31, 1962, page 5.

6. Ibid., page 6.

7. Midpoint Report, NASA CR-54046, Contract NAS 3-2796, April 20, 1964, page 1.

8. Ibid., page 7.

9. Ibid., page 14.

10. Fourth Quarterly Report, Contract NAS 7-202, October 30, 1963, page 23.

11. D. M. Perkins and E. F. Pasierb, Proc. of Fourth Photovoltaic Specialists Conference, Vol. II, A-2 (1964).

12. Fourth Quarterly Report, Contract NAS 7-202, October 30, 1963, pages 11, 12.

13. D. Perkins, private communication.

14. Midpoint Report, NASA CR-54046, Contract NAS 3-2796, April 20, 1964, page 5.

15. Ibid., page 23.

16. Ibid., page 25.

17. D. J. Harvey and N. E. Heyerdahl, Bull. Am. Phys. Soc. II <u>9</u>, 257 (1964).

18. J. E. Davey and T. Pankey, J. Appl. Phys. <u>35</u>, 2203 (1964).

19. J. L. Richards, P. B. Hart, and L. M. Gallone, J. Appl. Phys. <u>34</u>, 3418 (1963).

20. E. K. Müller, J. Appl. Phys. <u>35</u>, 580 (1964).

21. M. H. Francombe and M. M. Schlacter, "Growth Effects in Epitaxial Films of Au and InSb Prepared by Sputtering," Eleventh National Vacuum Symposium, September 29 to October 2, 1964, Chicago, Ill.

22. D. T. F. Marple, J. Appl. Phys. <u>35</u>, 1241 (1964).

REFERENCES (con't.)

23. T. P. McLean, Progress in Semiconductors 5. Edited by A. F. Gibson
     (John Wiley and Sons, Inc., New York, 1960) pp. 73-76.

24. H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Lett. 8,
     59 (1962).

25. M. D. Sturge, Phys. Rev. 127, 768 (1962).

26. R. P. Howson, Jour. Physique 25, 212 (1964).

27. K. G. Günther, Naturwiss. 45, 415 (1958).

28. L. W. Aukerman and R. D. Graft, National Symposium on Space Environment
     of Materials, May 7, 1962, St. Louis, Mo.

29. R. H. Bube, J. Appl. Phys. 31, 315 (1960); J. Blanc, R. H. Bube, and
     H. E. MacDonald, J. Appl. Phys. 32, 1666 (1960).

30. Midpoint Report, NASA CR-54046, Contract NAS 3-2796, April 20, 1964, page 9.

31. Ibid., page 12.

32. Ibid., page 16.

33. F. Seitz, Imperfections in Nearly Perfect Crystals (John Wiley and Sons,
     Inc., New York, 1952) p. 13.

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